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THE FORMATION AND DECOMPOSITION OF NICKEL CARBIDE IN EVAPORATED NICKEL FILMS ON GRAPHITE*

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Auger electron spectroscopy and X-ray photoelectron spectroscopy were used to study nickel carbide (Ni_3C) formed during the evaporation of nickel onto the surface of single-crystal graphite. It is shown that Ni_3C formed in this manner extends from the surface to close to the interface. A model is proposed to explain the mechanism of Ni_3C formation. The 1s photoelectron peak from Ni_3C is observed to have a binding energy 0.6 eV lower than that of pure graphite. This is attributed to the lack of any significant ionic bonding in Ni_3C.

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1. INTRODUCTION

In two previous publications[1,2] we reported the formation of nickel carbide (Ni_3C) thin films on the surface of single-crystal pyrolytic graphite. Auger electron spectroscopy (AES) was used to study the formation and thermal decomposition kinetics of the carbide film. The carbide was identified on the basis of the carbon Auger signal line shape[3,4]. In the present work X-ray photoelectron spectroscopy (XPS) and in-depth AES were used to gain further insight into the type of chemical bonding between nickel and carbon and to determine the composition of the interface.

2. EXPERIMENTAL

The experimental arrangement has been described previously[2]. A Physical Electronics model 545 electron spectroscopy for chemical analysis (ESCA)–AES analyzer was used. The XPS was performed using a magnesium anode.

3. RESULTS

Figure 1 shows the three types of carbon Auger signals observed during the deposition of nickel on graphite. Figure 1(a) corresponds to clean graphite. The carbon Auger signal in Fig. 1(b) corresponds to a mixture of graphitic and carbide type, representing the transition stage, as shown by Mojica and Levenson[5]. This
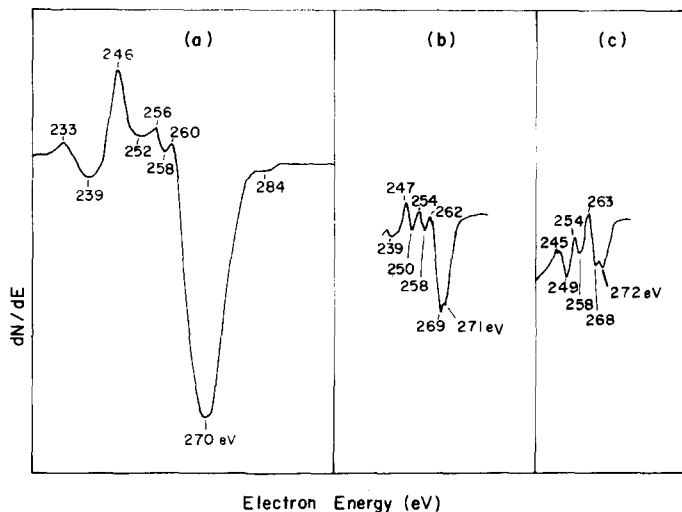

Fig. 1. The Auger spectra of (a) clean graphite, (b) carbon after fourteen monolayers of nickel have been deposited on the graphite surface and (c) carbon after thirty monolayers of nickel have been deposited on the graphite surface.

type of signal was observed after about fourteen monolayers of nickel had been deposited on the graphite surface, in accordance with the previous[1,2] results. The carbon Auger signal in Fig. 1(c) is due to Ni_3C, corresponding to complete carburization of nickel. This type was observed after about thirty monolayers had been deposited.

In order to determine the depth to which the nickel films were carburized, slow argon ion sputtering (about 7 Å min^{-1}) was performed with simultaneous monitoring of the carbon Auger peak shape and the peak-to-peak heights of the carbon, nickel and oxygen Auger signals. The results are shown in Fig. 2. The carbon signal was carbide type in region A, mixed in region B and graphitic in region C. It thus appears that, for a nickel film of this thickness, carburization is nearly complete, the carbide extending from the surface to close to the interface. Oxygen was present only in the surface region, as can be seen in Fig. 2.

As has been shown in our previous publication[2], metastable Ni_3C undergoes thermal decomposition on annealing, the time needed for complete conversion depending on the anneal temperature. In order to determine the extent of decomposition in the interior of the Ni_3C film, it was sputter profiled after thermal decomposition of the surface was observed. For annealing temperatures lower than 400 °C the carbon signal changed from graphitic to carbide type after two monolayers were sputtered off the surface. For annealing temperatures higher than 400 °C the carbon signal remained graphitic until the interface, indicating complete decomposition of the carbide film. This behavior was independent of the form of the initial Ni_3C, partially carburized (Fig. 1(b)) or fully carburized (Fig. 1(c)).

Repeated use of the same graphite sample for these studies (cleaned by annealing at 1300 °C prior to each fresh deposition) caused significant changes in the Auger line shape of the carbon signal after the deposited nickel film had been decomposed by annealing at 400 °C. The resulting carbon signal, though graphitic
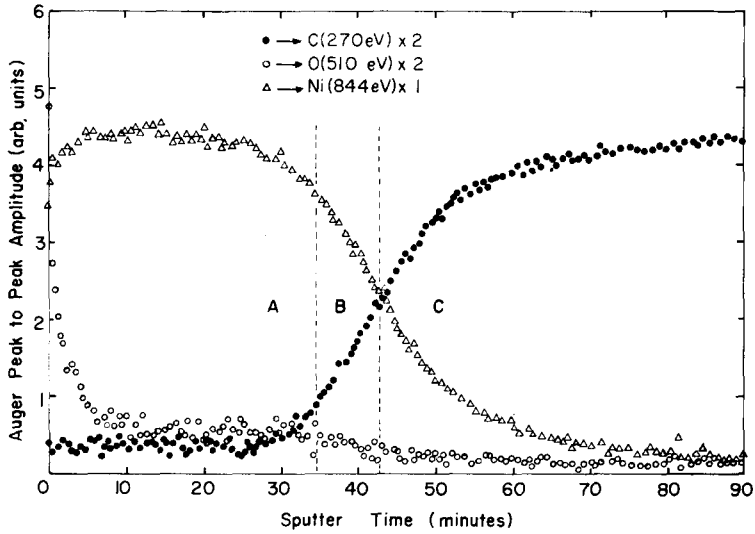
Fig. 2. The Auger depth profile of a nickel film deposited on single-crystal pyrolytic graphite. The carbon signal is carbide type in region A, mixed in region B and graphitic in region C.

in shape, showed a minimum at 278 eV, as can be seen in Fig. 3. This particular graphite sample had been used fifteen times prior to this evaporation. Another effect of repeated use of a graphite sample for nickel evaporation was that with each evaporation the sputter profile became longer, indicating increased interdiffusion or increased surface roughness.
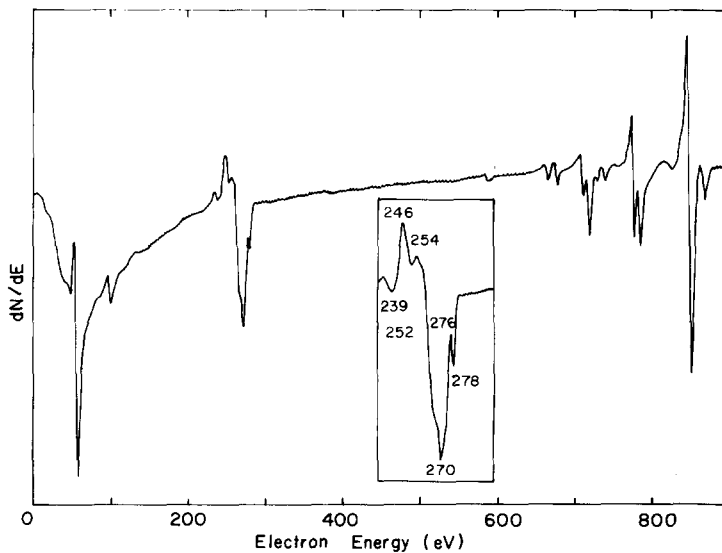

Fig. 3. The Auger spectrum of a nickel film on graphite after annealing at 400 °C for 30 min. The magnified carbon signal is shown in the inset on an expanded energy scale.

XPS spectra of carbon before deposition of the nickel film on the graphite and after formation of an Ni_3C film are shown in Fig. 4. The energy scale for these measurements was calibrated so that the electron binding energy for the 1s level of graphite is[6] at 284.6 eV. The 1s photoelectron peak of carbon from Ni_3C appears at 284.0 eV, which is shifted by 0.6 eV from that of clean graphite. The peak at 291 eV is the shake-up satellite[7] of the carbon 1s transition and that at 276 eV corresponds to excitation by Mg Kβ X-rays. No shift was detected in the nickel photoelectron energies.
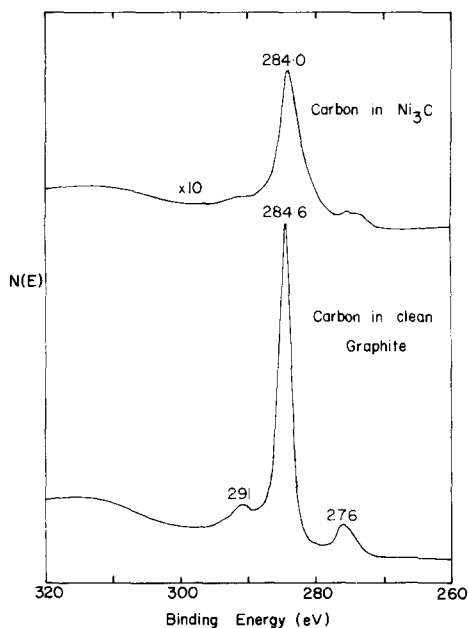

Fig. 4. Carbon 1s photoelectron spectra from clean graphite and Ni_3C.

4. DISCUSSION

4.1. Auger electron spectroscopy results

A comparison of the Auger spectra of carbon from the two carbide states (mixed and pure) shown in Fig. 1(b) and Fig. 1(c) reveals that, although the relative sizes of the minima in the spectra are quite different in the two cases, there is very little change in their energies. This is why the thermal decomposition kinetics obtained from the Ni_3C mixed with graphite were identical with those from pure Ni_3C.

A model can now be proposed to describe the mechanism of formation of Ni_3C in the nickel film deposited on graphite. We have shown previously[1] that nickel deposits in the form of islands during evaporation onto the graphite surface. Mojica and Levenson[5] observed carbon on the surface of 99.99% pure polycrystalline nickel ribbon after it had been annealed at 1000 °C for 30 min. Although they did not identify it as such, the carbon Auger signal corresponded[3] to that of Ni_3C. On annealing the nickel ribbon at temperatures ranging from 345

to 425 °C, they observed gradual transformation of the carbon signal from carbide type to graphitic type, which indicated the dissociation of the Ni_3C. Their studies showed clearly that there is a significant amount of bulk-to-surface precipitation and surface diffusion of carbon in polycrystalline nickel at these temperatures. The proposed mechanism for the formation of Ni_3C in our case is based on these results.

As described previously, the nickel evaporator in our case consisted of 99.99% pure nickel ribbon wrapped around a tungsten wire 2×10^{-2} in in diameter. The graphite sample was positioned about 1 cm from the evaporator, and nickel was evaporated slowly (about 1 Å min^{-1}) by resistively heating the tungsten wire. The temperature of the tungsten wire was estimated to be about 1200 °C and that of the graphite sample was slightly above 100 °C during evaporation. Since the time required for deposition of fourteen monolayers of nickel was 70 min, it can be assumed that there was some diffusion of carbon from the substrate to the nickel surface during this time and that this carbon reacted with nickel to form Ni_3C. The reason for the mixed type of carbon signal (Fig. 1(b)) at this point is that, because of island growth of nickel, some of the graphite substrate was also detected by AES. Since the surface temperature was low, no decomposition was observed during the evaporation time. During further evaporation of up to thirty monolayers of nickel, surface diffusion of carbon occurred in addition to the bulk-to-surface precipitation. As a result, the carbon signal acquired the fully carbide form shown in Fig. 1(c) and the substrate could no longer be detected by AES.

As has been shown in Fig. 3, repeated use of the same graphite sample for nickel evaporation produced some additional structures in the carbon Auger spectrum after the Ni_3C film had been decomposed by annealing at 400 °C. Although the carbon spectrum appears graphitic on the low energy side, there is a minimum at 278 eV which is connected with the presence of nickel on the surface. If all the nickel on the surface is desorbed by heating the sample to 1300 °C, the carbon signal assumes the pure graphitic form of Fig. 1(a). The spectrum of Fig. 3 thus appears to be due to a mixture of graphite and some sort of carbon–nickel compound. It is possible that, because of repeated sputtering and subsequent roughening of the graphite surface, its reactivity increases. Ni_3C formed on such a surface probably decomposes through the formation of an intermediate carbide[8] such as Ni_6C. The minimum at 278 eV could be characteristic of this intermediate carbide. Although the formation of Ni_6C during the decomposition of Ni_3C has been discounted by Hofer et al.[9], this seems to be the most plausible explanation for the fine structures observed in the carbon signal of Fig. 3. It is known that for some transition metal carbides such as VC and Cr_3C_2 the carbon Auger signal does show[10] an extra minimum at about 276 eV.

4.2. X-ray photoelectron spectroscopy results

As shown in Fig. 4, the binding energy of carbon 1s photoelectrons from Ni_3C is 0.6 eV lower than those from clean graphite. This shift is very small compared with the value of about 3 eV for stable transition metal carbides such as TiC, VC, HfC etc., as reported by Ramqvist[11]. The energy shift of the core electron level is a linear function of the charge transfer in the compound. On that basis, very little

charge transfer appears to take place in Ni_3C. The ionic character of Ni–C bonding appears to be negligible in this case. Most of the bonding is probably of a loose covalent type, resulting from an interaction between the carbon 2p and nickel 3d–4s orbitals. The carbon 2p and nickel 3d–4s valence photoelectrons should be studied in detail to gain further insight into the nature of chemical bonding in Ni_3C.

5. SUMMARIZING REMARKS

We showed that Ni_3C formed during the slow evaporation of nickel onto the surface of single-crystal graphite is not confined to the surface region but extends from the surface to close to the interface. A model was proposed to explain the mechanism of Ni_3C formation. A plausible explanation was given for the fine structures obtained in the carbon Auger spectrum during decomposition of the carbide. XPS was used to study the chemical bonding in Ni_3C. The unstable nature of this carbide can be explained by the lack of ionic bonding and the presence of loose covalent bonding.

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